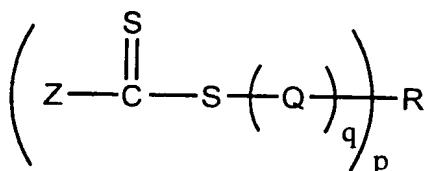


WHAT IS CLAIMED IS:

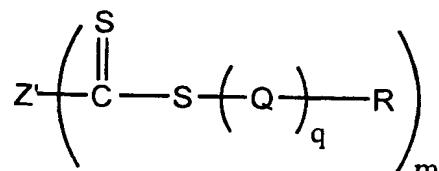
1. A process for the synthesis of polymers selected from the group consisting of:

5



Formula A

and

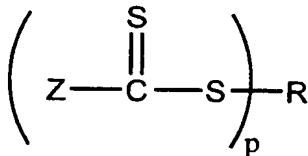


Formula B

comprising contacting:

10 (i) a monomer having repeating units, Q, selected from the group consisting of vinyl monomers of structure $\text{CH}_2=\text{CUV}$, maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

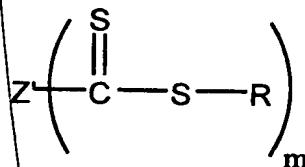
(ii) a thiocarbonylthio compound selected from:



Formula C

15

and



Formula D

having a chain transfer constant greater than about 0.1; and

20

(iii) free radicals produced from a free radical source; and
controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

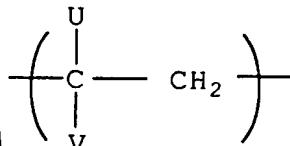
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the polymer of Formula B being made by contacting (i), (ii) D and (iii);

5 wherein:

Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy carbonyl, optionally substituted aryloxy carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O₂CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato [-P(=O)R"2], and a polymer chain formed by any mechanism;

15 Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



and

20 repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aroyloxy (O₂CR"), alkoxy- carbonyl and aryloxy-carbonyl (CO₂R");

V is selected from the group consisting of hydrogen, R", CO₂H, CO₂R", COR", CN, CONH₂, CONHR", CONR"2, O₂CR", OR" and halogen;

4 R is selected from a group consisting of optionally substituted alkyl; an
optionally substituted saturated, unsaturated or aromatic carbocyclic or
heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy;
optionally substituted dialkylamino; an organometallic species; and a polymer
5 chain prepared by any polymerization mechanism; in compounds C and D, R• is a
free-radical leaving group that initiates free radical polymerization;

10 R" is selected from the group consisting of optionally substituted C₁-C₁₈
alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents
are independently selected from the group that consists of epoxy, hydroxy, alkoxy,
acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-
carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

15 q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when p≥2 then R=R';

m is an integer ≥2; and

20 R' is a p-valent moiety selected from a member of the group consisting of
optionally substituted alkyl, optionally substituted aryl and a polymer chain; where
the connecting moieties are selected from the group consisting of aliphatic carbon,
aromatic carbon, silicon, and sulfur; in compounds C and D, R'• is a free radical
leaving group that initiates free radical polymerization.

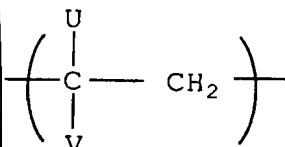
PCT/US97/12540

2. A process according to Claim 1 comprising controlling polydispersity by varying the ratio of the number of molecules of (ii) to (iii) as follows:

5 (a) lower polydispersity by increasing the ratio of (ii) to (iii); and
 (b) increase polydispersity by decreasing the ratio of (ii) to (iii).

3. A process according to Claim 2 comprising increasing the ratio of (ii) to (iii) and obtaining a polymer having a polydispersity below about 1.5.

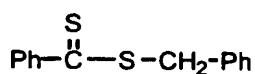
10 4. A process according to Claim 1 comprising selecting the following monomer repeating unit:



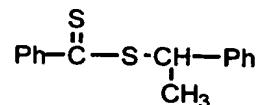
from (i).

15 5. A process according to Claim 1 comprising selecting the monomer units Q and the value of q so that when $q \geq 1$ and Q is a single monomer species, then the polymer is homopolymer; when $q \geq 2$ and Q is selected from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and when
 20 $q \geq 2$ and Q is selected from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then the polymer is block copolymer.

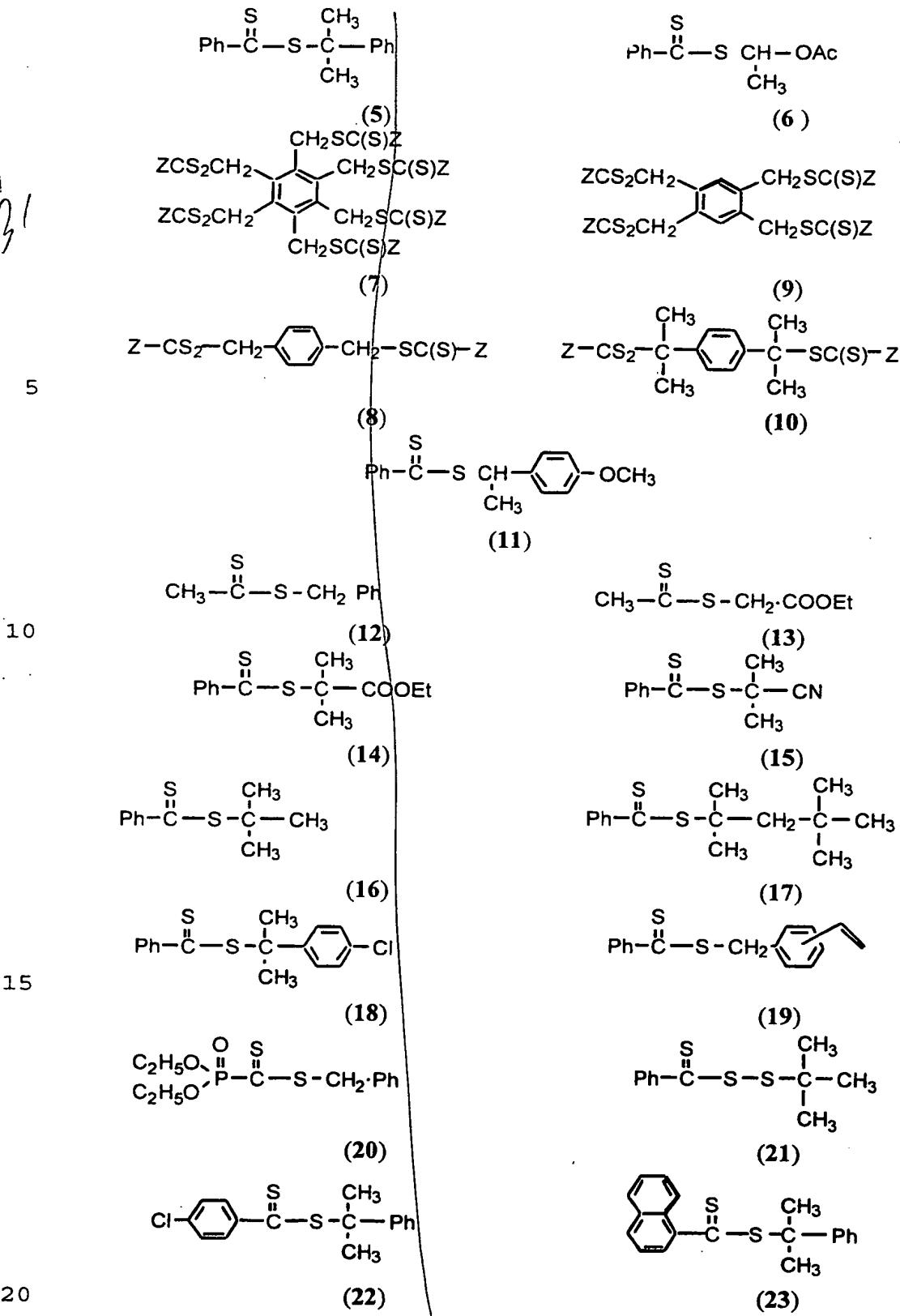
25 6. A process according to Claim 1 wherein the thiocarbonylthio compound is selected from the group consisting of:

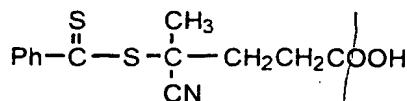


(3)

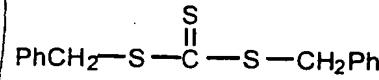


(4)

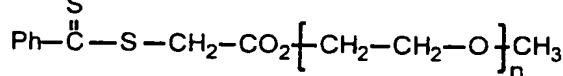
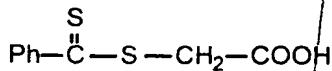




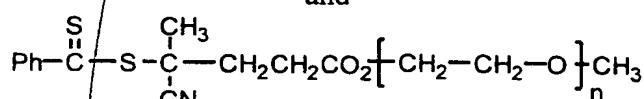
(24)



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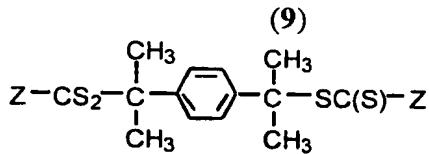
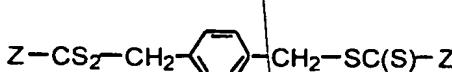
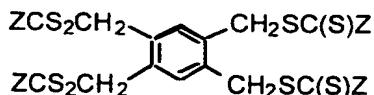
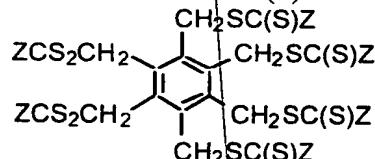
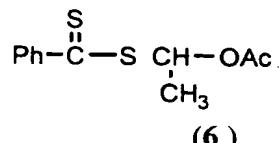
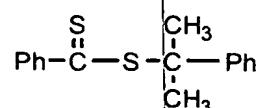
and



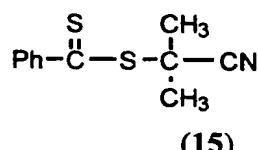
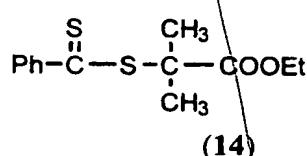
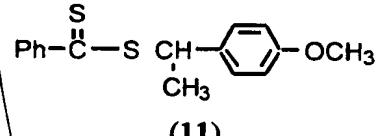
10 wherein Z is phenyl.

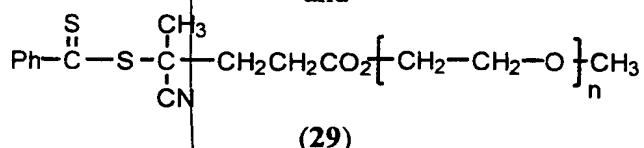
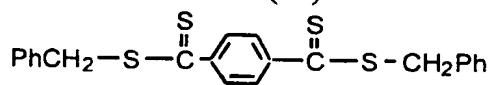
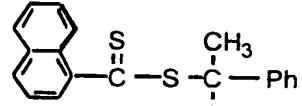
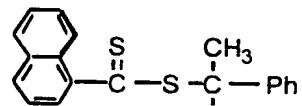
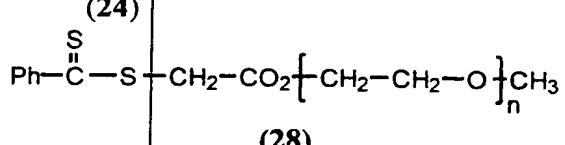
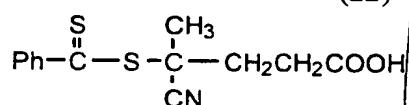
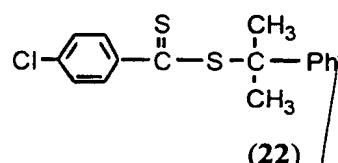
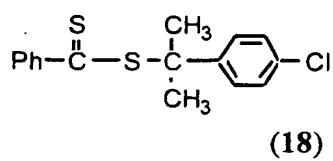
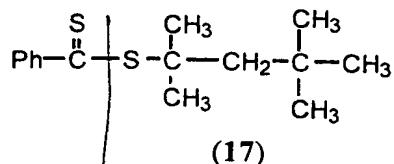
7. A chain transfer agent selected from the group consisting of:

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20





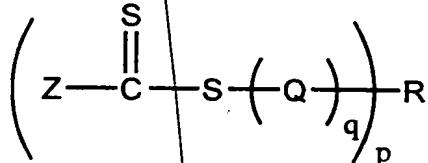
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and

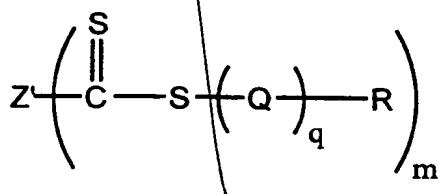
15

wherein Z is phenyl.

8. A polymer of the Formula



20 and

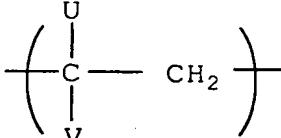


wherein:

B 5 Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy carbonyl or optionally substituted aryloxy carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O₂CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl- phosphinato [-P(=O)R"2], and a polymer chain formed by any mechanism;

10 Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

15 Q is selected from the group consisting of



 and

repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

20 U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl, wherein the substituents are independently selected from the group consisting of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aroyloxy (O₂CR"), alkoxy-carbonyl and aryloxy-carbonyl (CO₂R");

25 V is selected from the group consisting of hydrogen, R", CO₂H, CO₂R", COR", CN, CONH₂, CONHR", CONR"2, O₂CR", OR" and halogen;

30 R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; R• being derived from a free radical leaving group that initiates free radical polymerization;

β
5 R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

10

p is 1 or an integer greater than 1; when p≥2, then R=R';

m is an integer ≥2; and

15

R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; R'[•] being derived from a free radical leaving group that initiates free radical polymerization.

20

9. A polymer according to Claim 8 selected from the group consisting of random, block, graft, star and gradient copolymer.

10. A polymer according to Claim 9 having end group functionality.

Add A3